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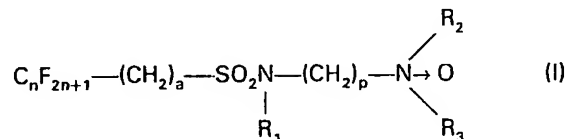GB 1302612
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(54) Amine oxides and fire-extinguishing compositions containing such amine oxides

(57) The amine oxides of the general formula:

$$C_nF_{2n+1}\text{---}(CH_2)_a\text{---}SO_2N\text{---}(CH_2)_p\text{---}N \rightarrow O \qquad (I)$$

with R_1 below N, and R_2, R_3 on the terminal N.

wherein
  n is an integer from 1 to 10
  a is an integer from 2 to 10
  p is an integer from 0 to 10
  R_1 is either a hydrogen atom or a C_{1-6} alkyl radical and
  each of R_2 and R_3 independently represent a C_{1-6} alkyl radical, are useful
as surface-active agents, especially in fire-extinguishing compositions.
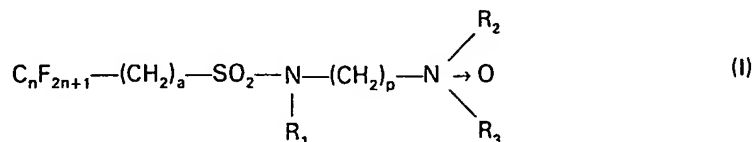
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SPECIFICATION
Amine oxides and fire-extinguishing compositions containing such amine oxides

This invention relates to new amine oxides of general formula (I):

$$C_nF_{2n+1}-(CH_2)_a-SO_2-\underset{\underset{R_1}{|}}{N}-(CH_2)_p-N\overset{\nearrow R_2}{\underset{\searrow R_3}{\rightarrow O}} \qquad (I)$$

5   wherein   5
     C_nF_{2n+1} represents a straight of branched perfluorinated chain where n is an integer from 1 to 20,
     a is an integer from 2 to 10,
     p is an integer from 0 to 10,
 R_1 is either a hydrogen atom or a C_{1-6} alkyl radical, and
10   R_2 and R_3 each independently represent a C_{1-6} alkyl radical.   10
     The amine oxides of general formula (I) in which a = 2, p = 3, each of R_2 and R_3 is a methyl radical
     and R_1 is hydrogen or a methyl radical are particularly interesting. The amine oxides of the invention
     may be prepared by the conventional methods of preparing amine oxides, for example by reacting the
     corresponding amines with hydrogen peroxide (cf. for example KIRK OTHMER 3rd edition, vol. 2, p.
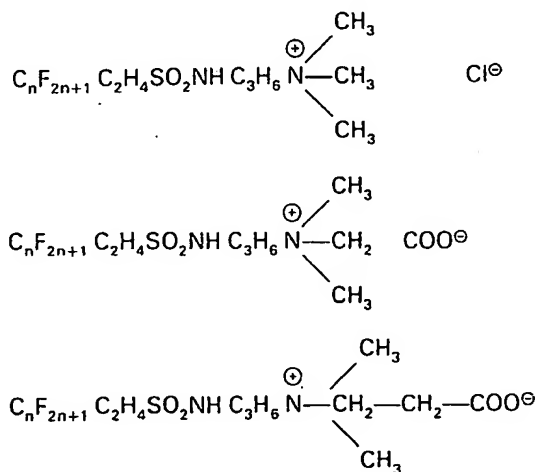15   259—271).   15
     The amines which may be used for preparing the amine oxides according to the invention are
     compounds of the general formula (II):

$$C_nF_{2n+1}-(CH_2)_a-SO_2-\underset{\underset{R_1}{|}}{N}\quad (CH_2)_p-N\overset{\nearrow R_2}{\underset{\searrow R_3}{}} \qquad (II)$$
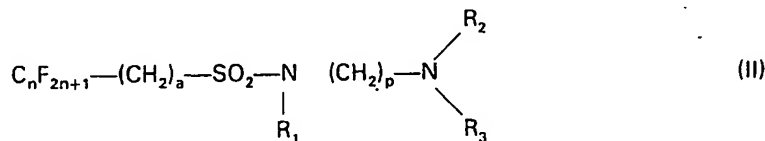
     wherein a, p, n, R_1, R_2 and R_3 are each as defined above, have previously been described by us, e.g. in
20   French Patent 2088594. These sulphamidoamines may constitute valuable raw materials for the   20
     production of fluorinated surfactants of the cationic or amphoteric type. Thus, French Patents 2084888,
     2088941, 2128028 and 2390426, described the surfactants obtained by quaternising these amines
     with alkyl halides, i.e. cationic surfactants, and the betaines obtained by quaternising these same
     amines with halogenocarboxylic acid salts, saturated aliphatic lactones of α-ethylene acids. The
25   following three formulae show characteristic examples of these different products: 25

$$C_nF_{2n+1}\ C_2H_4SO_2NH\ C_3H_6\ \overset{\oplus}{N}\overset{\nearrow CH_3}{\underset{\searrow CH_3}{-CH_3}} \qquad Cl^{\ominus}$$

$$C_nF_{2n+1}\ C_2H_4SO_2NH\ C_3H_6\ \overset{\oplus}{N}\overset{\nearrow CH_3}{\underset{\searrow CH_3}{-CH_2}}\quad COO^{\ominus}$$

$$C_nF_{2n+1}\ C_2H_4SO_2NH\ C_3H_6\ \overset{\oplus}{N}\overset{\nearrow CH_3}{\underset{\searrow CH_3}{-CH_2-CH_2-COO^{\ominus}}}$$

     These fluorinated surfactants will substantially reduce the surface tension of aqueous solutions
30   and can thus be used as wetting agents, foaming agents, emulsifiers or dispersants. Owing to the   30
     substantial reduction in surface tension which they bring about in water, these products have also been
     used for the production of surface-active compositions for use as bases in the production of
     extinguishing compounds intended for combating hydrocarbon fires.
     The applicant has found that the amine oxides according to the invention have significantly better
35   surface-active properties than the cationic or amphoteric products mentioned hereinbefore. These   35

differences are illustrated by the results of measurements of the reduction in the surface tension of aqueous solutions as shown in Table I.

TABLE I

No.	Fluorinated Product	Surface tensions of aqueous solutions containing 0.1% of fluorinated products in dynes /cm at 20°C
1	$C_6F_{13}C_2H_4SO_2NHC_3H_6\overset{\oplus}{N}$ —CH$_3$, —CH$_3$, —CH$_3$ Cl$^{\ominus}$	27
2	$C_6F_{13}C_2H_4SO_2NHC_3H_6\overset{\oplus}{N}$ —CH$_3$, —CH$_2$—COO$^{\ominus}$, —CH$_3$	17
3	$C_6F_{13}C_2H_4SO_2NHC_3H_6\overset{\pm}{N}$ —CH$_3$, —CH$_2$—CH$_2$—COO$^{\ominus}$, —CH$_3$	17
4	$C_6F_{13}C_2H_4SO_2N(CH_3)C_3H_6\overset{\oplus}{N}$ —CH$_3$, —CH$_2$—COO$^{\ominus}$, —CH$_3$	16.8
5	$C_6F_{13}C_2H_4SO_2NHC_3H_6N$ —CH$_3$, →O, —CH$_3$	13.4

The good surface-active properties of the amine oxides according to the invention can also be
demonstrated by their ability to form a film on the surface of a hydrocarbon when an aqueous solution
of surfactant is placed on the hydrocarbon. From French Patents 1405794 and 2009827, it is known
that the aqueous solutions of surfactants which form a film on the surface of hydrocarbons can be used
as extinguishing agents. The film-forming power of an aqueous surfactant solution is related to its
surface tension γ_B, the surface tension of the hydrocarbon γ_A and the interface tension γ_{AB} between the
two media by the equation

$$S = \gamma_A - (\gamma_B + \gamma_{AB})$$

The higher the positive value of the coefficient of spreading S, the better is the film-forming power.
Thus, aqueous surfactant solutions having low surface tension and low interface tension relative to the
hydrocarbon will spread better.

The efficacy of a film-forming extinguishing agent depends particularly on the speed of spreading
of the film. This can be evaluated by measuring the time taken by a certain volume of surface-active
solution to cover entirely a certain surface area of hydrocarbon. The speed of spreading can be
determined by the following method:

A glass dish 120 mm in diameter is half-filled with the reference hydrocarbon. 0.1 cm^3 of the
surfactant solution is placed in the centre of the hydrocarbon layer. The difference in reflecting power

makes it possible to follow the progress of the fluorinated film and thus measure the time required, in
seconds, to cover the surface completely. This spreading test is carried out with solutions of surfactants
at different concentrations (expressed in mg of fluorine per $100\,cm^3$ of solution) in fresh water and in
sea water. Three reference solvents were used, with different surface tensions:

5

$$\text{cyclohexane} : \quad \gamma_A = 25.3 \text{ dynes/cm at } 20°C$$

$$\text{petrol F} : \quad \gamma_A = 22.4$$

$$\text{m-hexane} : \quad \gamma_A = 18.4$$

When the reference solvent is petrol F or hexane, on which spreading is more difficult than on
cyclohexane, the volume of solution placed on the solvent is increased to $0.5 \, cm^3$.

10   The sea water used for these tests is synthetic sea water having the following composition:

1.1 % $MgCl_2.6H_2O$

0.16% $CaCl_2.2H_2O$

0.4 % Na_2SO_4

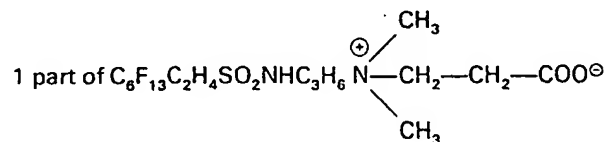2.5 % NaCl

15   95.84% distilled water

The amine oxide corresponding to product no. 5 of Table I has excellent film-forming properties
illustrated by the spreading speed test, the results of which are indicated in Table II. The times required
to obtain total spreading are indicated in seconds and the letter p means that only partial spreading
occurred.

TABLE II

Concentration of surfactant solution mg fluorine /100 cm³	Fresh water solution		Sea water solution	
	cyclohexane	petrol F	cyclohexane	petrol F
86	11.5	19.5	22.5	36.5
69	14	21	26	43
52	18.5	27.5	40	p
34	p	p	p	—

Although no spreading occurs on hexane at all, even at a concentration of 250 mg of fluorine per
100 cm³ of solution, these results can be regarded as excellent, since in practice the majority of the
fluorinated surfactant compounds described in the literature will not form durable films on hydrocarbons
whose surface tension is lower than that of cyclohexane. Thus, products nos. 2 and 3 in Table I do

25 not form a film on petrol F, and only spread out completely on cyclohexane for concentrations of 86 and   25
69 mg of fluorine per 100 cm³ and in periods of 40 to 60 seconds.

The amphoteric derivatives such as products nos. 2, 3 and 4 in Table I thus cannot be used as they
are in extinguishing compositions. On the other hand, it is possible to use them for this purpose by
combining them, for example, with other fluorinated surfactants. Compositions of this kind are

30 described in French Patent 2308674. It is also possible to use them in conjunction with non-fluorinated   30
surfactants such as those described in French patent 2009827. In fact, the addition of a non-fluorinated
surfactant to an aqueous solution of a fluorinated surfactant makes it possible to lower the interface
tension between the aqueous solution and the hydrocarbon and to increase the coefficient of spreading.
Different types of hydrocarbonated surfactants can thus be used to improve the spreading of aqueous

35 solutions of fluorinated surfactant on hydrocarbons and both ionic and non-ionic surfactants may give   35
good results. This synergy between fluorinated and non-fluorinated surfactants can be illustrated by
the film-forming power shown in Table III of an aqueous composition consisting of:

$$1 \text{ part of } C_6F_{13}C_2H_4SO_2NHC_3H_6 \overset{\oplus}{N}\!\!\!\overset{\diagup CH_3}{\underset{\diagdown CH_3}{}}\!\!\!-CH_2-CH_2-COO^{\ominus}$$

and three parts of non-ionic surfactant sold under the trade mark TRITON X 100 (ethoxylated octylphenol with 10 ethylene oxide groups made by Messrs. ROHM & HAAS).

TABLE III

Concentration of fluorinated surfactant expressed in mg fluorine /100 cm³	Fresh water solution		Sea water solution	
	Cyclohexane	Petrol F	Cyclohexane	Petrol F
86	3.5	5	1.5	2.5
69	3	10	1.5	2.5
52	5	19	2	3.5
54	9	p	4	9.5
17	p	—	p	p

5   At a concentration of 86 mg of fluorine per 100 cm³ of solution, the above composition based on product no. 3 of Table I forms a film on hexane, but this film only spreads partially.   5

This considerable improvement in the spreading properties by the addition of a non-fluorinated surfactant is also true in the case of the amine oxides according to the invention and even under these conditions the film-forming properties of the amine oxides are very superior to those of the fluorinated 10   surfactants mentioned hereinbefore. Thus, an aqueous composition consisting of: 10

$$1 \text{ part of } C_6F_{13}C_2H_4SO_2NHC_3H_6 \; N\overset{\diagup CH_3}{\underset{\diagdown CH_3}{}}\!\!\!\!\rightarrow O \text{ and}$$
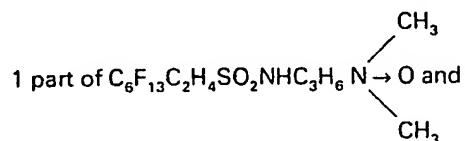
and 3 parts of Triton X 100 gave the spreading results shown in Table IV.

TABLE IV

Concentration of fluorinated surfactant expressed in mg fluorine /100 cm³	Freshwater solution		Sea water solution	
	Cyclohexane	Petrol F	Cyclohexane	Petrol F
86	1	1	1.5	1 5
69	1	1	1.5	1.5
52	1	1.5	2	2
34	1.5	1.5	4	4
17	11.5	11	15	10

· A comparison of Tables III and IV confirms the superiority of the amine oxides according to the invention, particularly as the last composition containing the amine oxide and the non-ionic surfactant spreads completely over hexane at a concentration of 86 mg of fluorine per 100 cm³ in 7.5 seconds in a fresh water medium and in 23 seconds in a sea water medium. The identical composition using the
5   amphoteric surfactant no. 3 of Table I instead of the amine oxide does not give total spreading over   5
hexane at the same concentration.

The superiority of the amine oxides over these amphoteric derivatives is all the more remarkable because the latter products can already be regarded as fluorinated surfactants which produce excellent extinguishing agents. The industrial product "Light Water FC 203" made by MINNESOTA MINING &
. 10 MANUFACTURING CO., which is probably one of the compositions most widely used in this field, has,   10
for example, with the same fluorine content, film-forming properties which are slightly less good than those of the amphoteric derivative combined with Triton X 100. On the other hand, its spreading results (Table V) are very significantly inferior to those of the amine oxides (Table IV).

TABLE V

Concentration of · of FC203 expressed in mg fluorine/100 cm³	Fresh water solution		Sea water solution	
	Cyclohexane	Petrol F	Cyclohexane	Petrol F
86	5 9	6.5	5	8.5
69	6.9	11.5	7	11
52	17	27.5	13	19
34	p	p	35 ·	50 ·
17	—	— ·	p	p

15   The amine oxides according to the invention can therefore be used in the field of extinguishing   15
agents of the AFFF type ("Aqueous Foam Forming Film"), particularly in combination with other fluorinated or non-fluorinated surfactants. The concentrate for the extinguisher may also contain other known additives such as foaming agents (hydrocarbonated surfactants), anti-freeze, solvents and foam stabilisers, chelating agents, corrosion inhibitors and electrolytes. The foam-generating component may
20   also be made up of protein hydrolysates, since these new surfactants are particularly compatible with   20
protein emulsifiers, owing to their chemical nature.
The following Examples further illustrate the invention.

EXAMPLE 1
100 g of 70% hydrogen peroxide are placed in a reactor containing 512 g of

$$C_6F_{13}C_2H_4SO_2NHCH_2CH_2CH_2\,N\diagup^{CH_3}_{\diagdown CH_3}$$

25   25
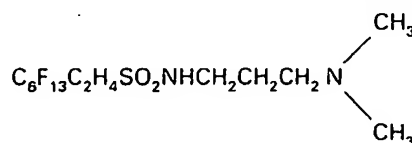
500 g of 95% ethanol and 200 g of water, with stirring, at 35°C. The mixture is then kept at this temperature, with stirring, for 24 minutes. Then 1 g of active charcoal is added and the mixture is refluxed for two hours. The mixture is then filtered, and by evaporation *in vacuo*, yields 547 g of a white solid which melts, with decomposition, at 135 to 138°C. The solid is identified by mass spectrometry,
30   infra-red spectrometry and by nuclear magnetic resonance as being the hydrated amine oxide of   30
formula:

$$C_6F_{13}C_2H_4SO_2NH{-}CH_2CH_2CH_2{-}N\to O, x\,H_2O \quad \diagup^{CH_3}_{\diagdown CH_3}$$
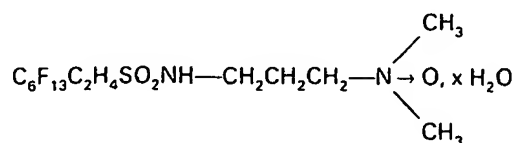
By chemical titration, i.e. by titrating this product with hydrochloric acid before and after

conversion of the residual amine into quaternary ammonium salt by reacting with methyl iodide, the following values were obtained:

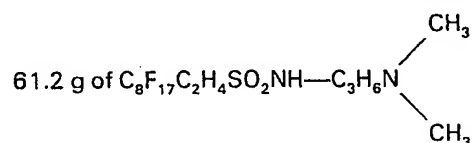| content of unconverted tertiary amine | : | <1% |
| content of amine oxide | : | 88.5% |

5   The surface tensions of aqueous solutions of this product are as follows at 20°C: 5

1,000 ppm of amine oxide	:	13.4 dynes/cm
100 ppm of amine oxide	:	13.4 dynes/cm
10 ppm of amine oxide	:	29 dynes/cm

The good spreading properties of this amine oxide are illustrated above in Tables II and IV.
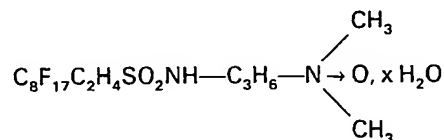
10 EXAMPLE 2   10
Following the same method as that described in Example 1, but using:

$$61.2 \text{ g of } C_8F_{17}C_2H_4SO_2NH—C_3H_6N \underset{CH_3}{\overset{CH_3}{<}}$$

50 g of 95% ethanol, 20 g of water and 20 g of 70% H_2O_2, 66 g of hydrated amine oxide of the formula

$$C_8F_{17}C_2H_4SO_2NH—C_3H_6—N \underset{CH_3}{\overset{CH_3}{<}} → O, x H_2O$$
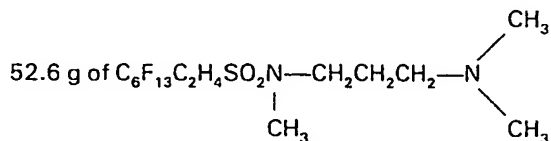
15 were obtained, titrating, by chemical analysis as 1% of unconverted residual amine and 85% of amine   15
oxide.
The surface tensions of aqueous solutions of this product, at 20°C, are as follows:
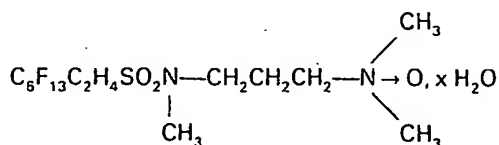
1,000 ppm of amine oxide	:	17 dynes/cm
100 ppm of amine oxide	:	21.9 dynes/cm
10 ppm of amine oxide	:	24.8 dynes/cm

20   20

EXAMPLE 3
Following the method of Example 1, but using:

$$52.6 \text{ g of } C_6F_{13}C_2H_4SO_2\underset{CH_3}{\overset{|}{N}}—CH_2CH_2CH_2—N \underset{CH_3}{\overset{CH_3}{<}}$$

50 g of 95% ethanol, 20 g of water, and 10 g of 70% H_2O_2, 57 g of hydrated amine oxide of the formula

25   25

$$C_6F_{13}C_2H_4SO_2\underset{CH_3}{\overset{|}{N}}—CH_2CH_2CH_2—N \underset{CH_3}{\overset{CH_3}{<}} → O, x H_2O$$

were obtained.
The surface tensions of aqueous solutions of this product at 20°C are as follows:

1,000 ppm of amine oxide   :   16.3 dynes/cm.

100 ppm of amine oxide   :   16.3 dynes/cm.

This product, in admixture with TRITON X 100 (3 parts TRITON X 100 to 1 part amine oxide), was tested as an extinguishing formulation, using the spreading test described above.

5   The results obtained are shown in Table VI.

TABLE VI

Concentration of amine oxide, expressed as mg of fluorine /100 cm^3	Fresh water solution		Sea water solution	
	Cyclohexane	Petrol F	Cyclohexane	Petrol F
86	1	1.5	1	1
69	1	2	1	1
52	1	2	1.5	1
34	2	4.5	2.5	2.5
17	15	p	14	17

EXAMPLE 4

Using the method described in Example 1, 50 g of 95% ethanol, 20 g of water, 10 g of 70% H_2O_2, and 57 g of

10

$$R_FC_2H_4SO_2NH—C_3H_6—N\begin{matrix} CH_3 \\ \\ CH_3 \end{matrix}$$
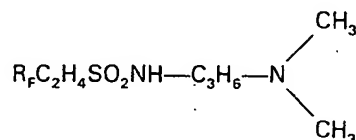
10

were reacted.

The sulphamidiamine used for this test is a mixture of different homologues, in which the fluorinated chain R_F contains 4 to 14 carbon atoms. The composition, by weight, of the product used was as follows:
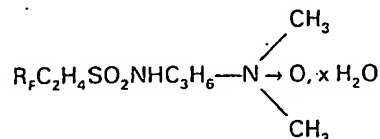
15   C_4F_9 derivate   1%   15

                      C_6F_{13} derivate   50

                      C_8F_{17} derivate   31

                      $C_{10}F_{21}$ derivate   10

                      $C_{12}F_{25}$ derivate   4

20                  $C_{14}F_{29}$ derivate   2   20

and the average molecular weight was 570.

In this way, 61 g of a white solid were obtained, identified as being the hydrated amine oxide of formula:

$$R_FC_2H_4SO_2NHC_3H_6—N \rightarrow O. x H_2O \begin{matrix} CH_3 \\ \\ CH_3 \end{matrix}$$

25 and titrating, by analysis, 82% of amine oxide. The free amine content was 1.6%. The surface tensions   25 of the aqueous solutions of this product are as follows, at 20°C:

1,000 ppm : 17 dynes/cm

100 ppm : 21.9 dynes/cm

10 ppm : 24.8 dynes/cm

The results of the spreading speed test described above for a mixture of 1 part of amine oxide and
5 3 parts of TRITON X 100 are given in Table VII.

TABLE VII

Concentration of amine oxide expressed in mg of fluorine /100 cm³	Fresh water solution		Sea water solution	
	Cyxlohexane	Petrol F	Cyclohexane	Petrol F
84	2	4	4.5	7
69	3	4.5	7.5	9
52	4	7.5	10.5	13.5
34	7.5	12.5	26.5	29
17	p	p	p	p

CLAIMS
    1. An amine oxide of the general formula:

$$C_nF_{2n+1}-(CH_2)_a-SO_2 \quad \underset{R_1}{N}-(CH_2)_p-\underset{R_3}{\overset{R_2}{N}} \to O \qquad (I)$$
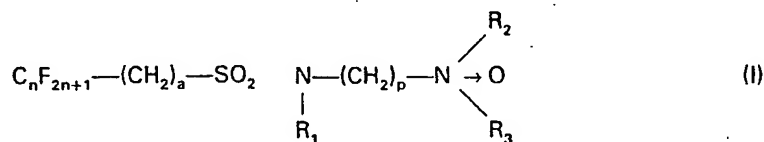
10 wherein:
    n is an integer from 1 to 10
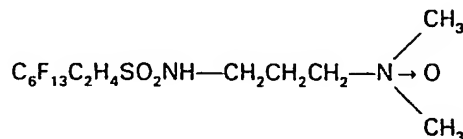   a is an integer from 2 to 10
    p is an integer from 0 to 10
    R_1 is either a hydrogen atom or a C_{1-6} alkyl radical and
15   each of R_2 and R_3 independently represent a C_{1-6} alkyl radical.
    2. An amine oxide according to Claim 1, wherein a is 2, p is 3, R_1 is a hydrogen atom or a methyl radical and each of R_2 and R_3 is a methyl radical.
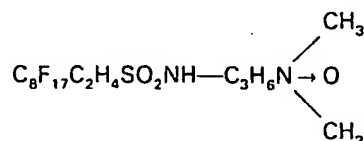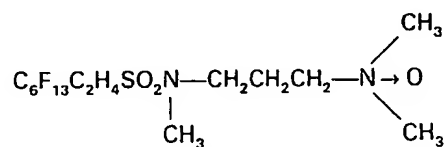   3. An amine oxide of formula:

$$C_6F_{13}C_2H_4SO_2NH-CH_2CH_2CH_2-\underset{CH_3}{\overset{CH_3}{N}} \to O$$

20   4. An amine oxide of formula:

$$C_8F_{17}C_2H_4SO_2NH-C_3H_6\underset{CH_3}{\overset{CH_3}{N}} \to O$$

    5. An amine oxide of formula:

$$C_6F_{13}C_2H_4SO_2N\!-\!CH_2CH_2CH_2\!-\!\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{\diagup}}{N}}\!\rightarrow O$$

6. An amine oxide of general formula (I) substantially as hereinbefore described in Example 4.

7. A surfactant composition incorporating an amine oxide as claimed in any one of the preceding claims.

5

8. A fire-extinguishing composition incorporating an amine-oxide as claimed in any one of the preceding claims.

5

9. A fire-extinguishing composition according to Claim 8, which also includes a fluorinated or non-fluorinated surface-active agent.

10. Use of an amine oxide according to any one of Claims 1 to 6 as surface active agents.

10

11. Use of an amine oxide according to any one of Claims 1 to 6 as surface active agents in extinguishing compositions.

10

12. Use of an amine oxide according to any one of Claims 1 to 6, in conjuction with other fluorinated or non-fluorinated surface active agents, as surface active agents in extinguishing compositions.